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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the new nonaqueous secondary battery which has the high capacity which uses the material which supported lithium beforehand for carbon negative electrode material.
[0002]
[Description of the Prior Art]The request to high-capacity-izing of a rechargeable battery becomes strong with the spread of a portable personal computer or cellular phones in recent years, The lithium ion nonaqueous secondary battery of composition of having used as the negative electrode the carbon material which emits [occlusion and] an anode and lithium for the lithium containing transition metal multiple oxide has come to take the post of the leading role of a small rechargeable battery from high tension and the feature that it is lightweight and an energy density is large. With expansion of cell demand, the demand of the high energy density from a user is becoming increasingly strong, and active material development which put high-energy-density-izing of a noncommercial cell and a future electromobile power supply into the view is furthered energetically.
[0003]The high capacity carbon material exceeding LiC_6 (372 mAh/g) which is active as for development of the carbon material used especially for the negative electrode, and is made into the theoretical limit of lithium occlusion these days also comes to be found out. Occlusion mechanisms, such as "it is generation of a lithium ion cluster to the opening in carbon", "generation of the lithium graphite lamellar compound of LiC2 presentation", "carbon of an aromatic molecule end and the covalent bond of lithium", and "generation etc. of the ion complex which consists of an aromatic molecule and a lithium ion", are proposed.
[0004]Improvement in the charge and discharge efficiency in early stages of a carbon material is very important for high-capacity-izing of a rechargeable battery with high-capacity-izing of a carbon material. Namely, when the charge and discharge efficiency in early stages of a carbon material is low, some lithium by which occlusion was carried out to the negative electrode by the charging process causes two or more irreversible side reactions and lithium does not return to an anode by a discharge process. Since it is necessary to build into a rechargeable battery too much the lithium contained metal oxide which is positive active material beforehand in order to compensate consumed lithium, rechargeable battery capacity lowering is brought about as a result. The raw material of an old carbon material, a firing condition, electrode sheet composition, electrolysis solution composition, Although optimization of the battery manufacturing process, etc. were advanced energetically and early charge and discharge efficiency has improved, have not yet

reached to 100%, and, The carbon material of a graphite system with early comparatively good charge and discharge efficiency has a fault to which early charge and discharge efficiency falls, when propylene carbonate is used as a solvent of an electrolysis solution.

[0005]As art which improves initial charge and discharge efficiency in a carbon material, lithium is already beforehand supported to a carbon material, a part for a charge-and-discharge loss is compensated, and aiming at improvement in initial charge and discharge efficiency is proposed. Supporting lithium beforehand to the carbon material which has the poly acene similar structure acquired by calcinating phenol resin under an inert atmosphere, and aiming at compensation for a charge-and-discharge loss is proposed by JP,5-28,985,A. The method of supporting lithium stops at the description, selection, suitably from publicly known methods, such as an electrolytic decomposition process, a gaseous phase method, a liquid phase process, and ion implantation, and the concrete example is not indicated. Future JP,5-28,986,A, 5-28,987, 5-29,023, Similarly the concrete indication is not shown about the proposal of 5-159,805, 5-159,806, 5-159,806, 5-325,965, 5-325,972, 6-20,722, and 6-203,833.

[0006]The indication of the concrete method for supporting lithium beforehand to the carbon material of JP,7-808,852,A (WO95/08852), Although it is the method of assembling a cell after doping lithium to a carbon material beforehand by the seal of approval of the potential below lithium metal potential using the electrochemical cell which made the lithium metal the counter electrode, and the method of assembling a cell after sticking a lithium metal on a negative electrode sheet, Also when [this] it is both a method, lithium was doped beforehand and processing to a rechargeable battery is performed under a highly precise drying atmosphere since a carbon negative electrode sheet has very high labile, it is difficult for degradation to secure the high energy density as an intention greatly. With the doped carbon negative electrode sheet, the remarkable fall of flexural strength especially takes place, in a cylindrical cell, winding of a negative electrode sheet is difficult and the rises of the internal resistance which originates in exfoliation of an electrode layer from a charge collector occur frequently. Thus, a carbon material has a serious obstacle on production of the cylindrical cell used for a portable personal computer or a cellular phone, or a square-shaped cell in the method of carrying out preliminary insertion of the lithium, and it is not desirable. Since the method indicated to JP,8-64,247,A after it, 8-64,248, 8-64,249, 8-64,250, 8-64,251, 8-64,252, 8-162,159, etc. also has the same difficulty substantially, it is not desirable.

[0007]Since a carbon material and lithium metal foil react with generation of heat and internal resistance rises, the method of creating a cell, after creating beforehand the negative electrode sheet which stuck lithium metal foil on both sides containing the carbon material of JP,8-64,247,A of the upper part of the periphery of a negative electrode sheet and the lower part directly is not preferred.

[0008]How to install disc-like lithium in the bottom of the battery can of JP,8-162,161,A, and carry out electrochemical doping of the lithium to a carbon material using contact with the end of a negative pole collector, Equalization of the lithium doping concentration to a negative electrode sheet is difficult, and it is not desirable in order for doping to take a long time. Since machining load also increases, it is not desirable.

[0009]The lithium decrement of the positive electrode sheet which moved to carbon negative electrode material by charge of JP,8-255,633,A, 8-255,634, and 8-255,635, The method of performing compensation through resistance within a cell serves as restrictions of manufacture [the increase in a member and a work process, uneven-izing of the lithium concentration to a positive electrode sheet, etc.] from the lithium metal installed in the cell. In the method of putting the lithium unit which embedded and created lithium metal foil

with the roller to the copper expanded metal of JP,9-102,328,A between negative electrodes, and assembling a cell. There are which restrictions with difficult lamination of a lithium unit with difficult lithium unit creation, and it is not desirable.

[0010]By the method of decreasing irreversible capacity, the first cycle efficiency is only 70 to 80% by using the electrolysis solution containing the carbonate which has an aromatic ring in the rechargeable lithium-ion battery which used graphite for the negative electrode active material proposed by JP,8-255,633,A.

[0011]Such much proposals support lithium beforehand to a carbon material, compensate a part for a charge-and-discharge loss, aim at improvement in initial charge and discharge efficiency, and show directly that the needs which high-capacity-ize a nonaqueous secondary battery are great.

[0012]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the high capacity nonaqueous secondary battery which supported lithium beforehand to the carbon material, compensated a part for a charge-and-discharge loss, and aimed at improvement in initial charge and discharge efficiency, and was excellent in productivity.

[0013]

[Means for Solving the Problem]A positive electrode sheet containing positive active material in which a technical problem of this invention made a subject a lithium containing transition metal multiple oxide, In a nonaqueous secondary battery which has nonaqueous electrolyte containing a negative electrode sheet and lithium salt containing a carbon material which emits [occlusion and] lithium, It is the composition that a metallic foil with which a negative electrode sheet made lithium a subject via an auxiliary layer was stuck beforehand, and a nonaqueous secondary battery containing at least one sort of hydrazine derivatives and/or aromatic compounds was able to attain to nonaqueous electrolyte.

[0014]

[Embodiment of the Invention]Hereafter, the nonaqueous secondary battery of this invention is explained in full detail. The nonaqueous secondary battery which has the high energy density which is the purpose of this invention, After the metallic foil which made lithium the subject creates the negative electrode sheet containing the carbon material installed via the auxiliary layer, A nonaqueous secondary battery is assembled with a positive electrode sheet and a separator, and after pouring in the electrolysis solution containing at least one sort of hydrazine derivatives, and/or aromatic compounds, preliminary support of lithium to a carbon material is substantially attained by aging. A desirable lithium reserve holding amount makes an index the quantity of an irreversible side reaction with lithium of a negative pole material, i.e., the charge and discharge efficiency of an initial cycle, and the optimum amount is chosen suitably.

[0015]Although aging of the 1st day to 20 days is preferred among 0-80 **, the 4th day to especially ten days are preferred among 20-60 **.

[0016]As long as the portion which sticks by pressure the metallic foil which made lithium the subject is on a negative electrode sheet, arbitrary positions may be sufficient as it. Although you make it pile each other up and it is preferred to pile up the metallic foil of thickness regularity all over a negative electrode sheet as for a pattern, superposition may also be used selectively not the whole negative electrode sheet surface but a stripe (length and width), frame shape, etc. Although the fixed thing of the interval of superposition of a stripe is preferred, I hope that it is not fixed. The pattern of the shape of a lattice which combined the lengthwise direction and the transverse direction can also be used. As a method of piling up the metallic foil which made

lithium the subject on a negative pole material, a roll replica method or a board replica method is used.
[0017]Once a roll replica method sticks on a roll the metallic foil cut in arbitrary sizes, it is the method of sticking on a negative electrode sheet continuously, carrying out a calendar press. Using a congruence roller sticks and a roll is preferred from a viewpoint on a disposition. Although the size of a roll may be arbitrary, it is preferred to use a thing 0.5-100 cm in diameter, and it is a 1-50-cm thing more preferably. The construction material of material of roll which cannot react to lithium easily is preferred, and its metal things, such as polymer, such as polyolefines (polyethylene, polypropylene, etc.), polyimide, and polycarbonate, stainless steel, molybdenum, are preferred. Once a board replica method sticks the metallic foil cut in arbitrary sizes on a flat surface, it is the method of sticking on a negative electrode sheet, pressing. The same thing as material of roll of the construction material of a board is preferred.
[0018]A thing desirable as a metallic foil which made lithium the subject, For example, it is Li-aluminum, Li-aluminum-Mn, Li-aluminum-Mg, Li-aluminum-Sn, Li-aluminum-In, Li-aluminum-Cd, etc., and things desirable as metal in which lithium and an alloy are possible are aluminum, aluminum-Mn, aluminum-Mg, aluminum-Sn, aluminum-In, etc., for example. As for the lithium content of a metallic foil, it is preferred that it is not less than 90%, and it is most preferred that it is not less than 98%. It is important from a homogeneous viewpoint and it is preferred that it is 1-100 micrometers, if the thickness of lithium foil is 5-50 micrometers or less, it is still more preferred and its about 10-40 micrometers are the most preferred.
[0019]In order to avoid the rapid reaction accompanied by generation of heat with a negative pole material, the metallic foil which made lithium the subject provides the auxiliary layer which does not contain a negative pole material including the particles of much more insoluble in water nature further at least any longer on a binder layer, and is stuck by pressure on it.
[0020]In this invention, the auxiliary layer provided in the negative electrode sheet consists of at least one layer, and may be constituted by congener or two or more layers of a different kind. These auxiliary layers may be insulating layers which do not have electron conductivity substantially, and may be conductive layers. It may be the gestalt which the conductive layer and the insulating layer laminated. As for the thickness of an auxiliary layer, 0.2 micrometers or more 40 micrometers or less are preferred, and 0.3 micrometers or more its 20 micrometers or less are more preferred. An auxiliary layer comprises an insulating particle of insoluble in water nature, a conductive particle of insoluble in water nature, and an organic polymer material. As an insulating particle of the insoluble in water nature of this invention, inorganic substance particles and organic matter particles can be mentioned.
[0021]As inorganic substance particles, cull KOGENAITO (for example, a sulfide, an oxide) of metal and a nonmetallic element, carbide, a silicide, and a nitride can be mentioned. In cull KOGENAITO, an oxide is preferred and the oxide which is hard to be returned is preferred.
[0022]As these oxides, for example aluminum$_2O_3$, As_4O_6, B_2O_3, BaO, BeO, CaO, Li_2O, K_2O, Na_2O, In_2O_3, MgO, Sb_2O_5, SiO_2, SrO, and ZrO_4 are mentioned. In these, aluminum$_2O_3$, BaO, BeO, CaO, K_2O, Na_2O, MgO, SiO_2, SrO, and especially ZrO_4 are preferred. These oxides may be independent or may be multiple oxides. As a compound desirable as a multiple oxide, mullite (3aluminum$_2O_3$ and 2SiO_2), A steatite (MgO-SiO_2), forsterite (2 MgO-SiO_2), cordierite (2MgO, 2aluminum$_2O_3$, and 5SiO_2), etc. can be mentioned. In carbide, silicide, and a nitride, SiC, alumimium nitride (AlN), BN, and BP have highly and chemically stable

insulation, and are preferred, and especially SiC using especially BeO, Be, and BN as a sintering auxiliary agent is preferred. By methods, such as control of a generation condition, and grinding, 0.1 micrometers or more, 20 micrometers or less, these insulating inorganic compound particles are made into a particle (0.2 micrometers or more and 15 micrometers or less), and are used especially preferably.

[0023]The powdery part of the latex over which the bridge was constructed as organic matter particles, or a fluoro-resin is preferred, and what does not decompose below 300 ** or does not form a coat is preferred. The impalpable powder of Teflon is more preferred.

[0024]Metal, a metallic oxide, and a metal fiber can be mentioned as a conductive particle of insoluble in water nature.

[0025]Copper, nickel, iron, molybdenum, titanium, tungsten, and tantalum in which reactivity with lithium cannot form an alloy easily low as metal powder are preferred. A needle and a column, tabular, and massive any may be sufficient as the form of such metal powder, 0.02 micrometers or more and 20 micrometers or less have a preferred overall diameter, and it is more preferred. [of 0.1 micrometers or more and 10 micrometers or less] That [their] in which the surface has not oxidized too much is preferred, and as for such metal powder, when having oxidized, heat-treating by reducing atmosphere is preferred.

[0026]As for the rate of the conductive particle contained in an auxiliary layer, 2.5 % of the weight or more and 96 % of the weight or less are preferred, it is more preferred, and is preferred. [of 10 % of the weight or more and especially 93 % of the weight or less] [of 5 % of the weight or more and 95 % of the weight or less]

[0027]The binder used when forming the electrode compound described later as an organic polymer material used with the particles and/or the conductive particles which do not have conductivity in the auxiliary layer of this invention substantially can be mentioned. 96 or less % of the weight of 40 % of the weight or more has preferred particles to both gross weight, and, as for the ratio of particles and organic polymer, 94 or less % of the weight of 50 % of the weight or more is more preferred.

[0028]After the painting method of an auxiliary layer paints the mixture which came lithium out of the material in which occlusion discharge is possible reversibly on the charge collector, and made the subject a certain metal or a half a carat fellows oxide, the serial method which paints an auxiliary layer one by one may be sufficient as it, and it may be a simultaneous coating method which paints a binder layer and an auxiliary layer simultaneously.

[0029]In order to aim at improvement in the charge and discharge efficiency in early stages of a carbon material, in addition to negative electrode sheet production by an above-mentioned method, the electrolyte which made at least one sort of hydrazine derivatives and/or aromatic compounds contain is used for the cell of this invention as an additive agent.

[0030]As for the hydrazine derivative added by the electrolysis solution, it is preferred that nitrogen is replaced by the alkyl group which is not replaced [substitution or], an aryl group, the heterocycle group, the acyl group, the oxycarbonyl group, and the sulfonyl group. The alkyl groups which are not replaced [desirable substitution or] are the total carbon numbers 1 thru/or 12, for example, methyl, ethyl, isopropyl, t-butyl, allyl, cyclohexyl, benzyl, etc. are mentioned. The aryl groups which are not replaced [desirable substitution or] are the total carbon numbers 6 thru/or 20, for example, phenyl, naphthyl, etc. are mentioned. The heterocycle groups which are not replaced [desirable substitution or] are the total carbon numbers 1 thru/or 12, for example, pyridyl, pyrazyl, quinolyl, a furil, thienyl, benzimidazolyl, indazolyl, etc. are mentioned. The acyl groups which are not replaced [desirable substitution or] are the total carbon numbers 1 thru/or 12, for

example, formyl, acetyl, pivaloyl, benzoyl, etc. are mentioned. The oxycarbonyl groups which are not replaced [desirable substitution or] are the total carbon numbers 1 thru/or 12, for example, carbomethoxy, t-butoxycarbonyl, benzyloxycarbonyl, phenoxycarbonyl, etc. are mentioned. As for a desirable sulfonyl group, methylsulfonyl, phenyl slufonyl, p-tosyl, etc. are mentioned, for example. As an example of the hydrazine derivative added by the electrolysis solution, 1,2-bis(carbomethoxy)-1,2-dimethylhydrazine, 1,2-bis (ethoxycarbonyl)-1,2-dimethylhydrazine, 1,2-bis(t-butoxycarbonyl)-1,2-dimethylhydrazine, 1,2-bis (ethoxycarbonyl)-1-methyl-2-phenylhydrazine, 1,2-bis(ethoxycarbonyl)-1,2-diphenylhydrazine, etc. are mentioned.

[0031]As an example of the aromatic compounds added by the electrolysis solution, Monocyclic aromatic compound compounds, such as benzenefranc thiophene pyridine, The acenes which consist of cyclic structures of the same kind, such as naphthalene anthracene. The hydrocarbon system aromatic compounds which have cyclic structures of a different kind, such as an indene fluorene, The aromatic compounds which have the oxygen content cyclic structure derived from dioxybenzenedihydroxynaphthalene dioxyanthracenes, such as catechol carbonate, etc., The aromatic compounds which have oxygen content aromatic rings, such as a benzofuran dibenzofuran, The aromatic compounds which have nitrogen content aromatic rings which have sulfur content aromatic rings, such as a thiophene benzothiophene dibenzo thiophene, such as aromatic compounds and pyridinequinolineacridine Indore carbazole, and these substitution products are mentioned.

[0032]Although the addition to the electrolyte of hydrazine and/or aromatic compounds can be chosen arbitrarily, it is 0.05 to 5 % of the weight that it is 0.01 to 10 % of the weight to the whole electrolyte desirable especially preferably.

[0033]To an electrolyte, other compounds may be added in order to improve discharge and a charging and discharging characteristic. For example, triethyl phosphite, triethanolamine, cyclic ether, Ethylenediamine, n-glyme, hexalin acid TORIAMIDO, ethylene glycol dialkyl ether, Quarternary ammonium salt, a polyethylene glycol, pyrrole, 2-methoxyethanol, $AlCl_3$, the triethylenephosphoramide, trialkylphosphine, The crown ether like morpholine, an aryl compound with a carbonyl group, and the 12-crown 4, hexamethylphosphoric triamide and 4-alkyl morpholine, the bicyclic third class amine, oil, the fourth class phosphonium salt, the third class sulfonium salt, etc. can be mentioned.

[0034]In order to make an electrolysis solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and 3 fluoridation ethylene chloride can be included in an electrolysis solution. In order to give fitness to high temperature preservation, carbon dioxide can be included in an electrolysis solution.

[0035]As a solvent which can be used by this invention, propylene carbonate, ethylene carbonate, Butylene carbonate, dimethyl carbonate, diethyl carbonate, Methylethyl carbonate, gamma-butyrolactone, methyl formate, methyl acetate, 1,2-dimethoxyethane, a tetrahydrofuran, 2-methyltetrahydrofuran, Dimethyl sulfoxide, 1,3-dioxolane, a formamide, dimethylformamide, Dioxolane, dioxane, acetonitrile, nitromethane, ethylmono- glyme, Trialkyl phosphate, trimethoxy methane, a dioxolane derivative, sulfolane, Aprotic organic solvents, such as 3-methyl-2-oxazolidinone, a propylene carbonate derivative, a tetrahydrofuran derivative, ethyl ether, and 1,3-propane Salton, can be mentioned, and these kinds or two sorts or more are mixed and used. In these, the solvent of a carbonate system is preferred and it is preferred especially to mix and use cyclic carbonate and non-cyclic carbonate. As cyclic carbonate, ethylene carbonate and propylene carbonate are preferred. As non-cyclic carbonate, diethyl carbonate, dimethyl carbonate, and

MECHIRUECHIRUKABONETO ** are preferred. As an electrolysis solution which can be used by this invention, ethylene carbonate, propylene carbonate, The electrolysis solution which contains $LiCF_3SO_3$, $LiClO_4$, $LiBF_4$, and/or $LiPF_6$ in the electrolysis solution which mixed suitably 1,2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate is preferred. Especially to at least one mixed solvent of propylene carbonate, at least one side of ethylene carbonate and dimethyl carbonate, or diethyl carbonate. A kind of salt selected from $LiCF_3SO_3$, $LiClO_4$, or $LiBF_4$ and the electrolysis solution containing $LiPF_6$ are preferred at least. The quantity in particular that adds these electrolysis solutions in a cell is not limited, but can be used according to the quantity of a positive electrode material or a negative pole material, or the size of a cell.

[0036]Although an electrolysis solution may pour in the whole quantity at once, it is preferred to pour in in 2 steps or more. When pouring in in 2 steps or more, the presentation (after pouring in the solution which dissolved lithium salt in the nonaqueous solvent or the nonaqueous solvent, the solution which dissolved lithium salt in the nonaqueous solvent or nonaqueous solvent whose viscosity is higher than said solvent is poured in) which is different also by the same presentation may be sufficient as each liquid. It may perform decompressing a battery can for shortening of the injection time of an electrolysis solution, etc., or applying a centrifugal force and an ultrasonic wave to a battery can.

[0037]The desirable carbon material used for the negative electrode of this invention, the carbon material (JP,62-122,066,A.) in which it is a charge of a difficulty graphitized carbon material, and a black lead system carbon material, and a spacing, density, and crystallite size were specified JP,2-66,856,A, 3-245,473, the mixture of natural graphite and an artificial graphite (JP,5-290,844,A), a vapor-phase-epitaxy carbon material (JP,63-24,555,A and 63-13,282.) 63-58,763, JP,6-212,617,A, and the MEZOFESU carbon material (JP,5-307,957,A.) compounded by pitch calcination Carbon materials, such as black lead (JP,6-84,516,A) which has 5-307,958, 7-85,862, 8-315,820, and an enveloping layer, can be mentioned.

[0038]the carbon material (West Mio: -- a Japanese ene RUGI academic journal.) produced as a carbon material by calcinating furfuryl alcohol resin (PFA) under an inert atmosphere with independent, or phosphorus compounds and a boron compound The difficulty black lead nature carbon material produced by calcinating the coal tar pitch by which PARAKI silylene glycol was added under an inert atmosphere in 71 volumes, 828 pages, and 1992, the difficulty black lead nature carbon material (Jay Earl Dern et al..) which has the poly acene similar structure acquired by calcinating phenol resin under an inert atmosphere the amorphous carbon material (a jar NARUOBU electrochemical society.) produced by calcinating meso carbon micro beads (MCMB) below 1000 ** under an inert atmosphere in carbon, 34 volumes, 1501 pages, and 1996 The amorphous carbon material (Morinobu Endo et al., carbon, 155 volumes, 315 pages, 1992) etc. which are produced by calcinating poly para-phenylene below 1000 ** under an inert atmosphere in 142 volumes, 1041 pages, and 1995 can be mentioned.

[0039]It is also possible to use together with a carbon material and to use non-oxide stock materials, such as silicon, germanium, tin, and lead, the inorganic oxide, or the inorganic chalcogenide which can form the intermetallic compound in which lithium and lithium were ionized.

[0040]The positive active material used by this invention is a lithium containing transition metal multiple oxide which can insert and emit a lithium ion reversibly.

[0041]As a desirable lithium containing transition metal multiple oxide, Contain lithium and And Ti, V, Cr, Mn, Fe, Co, nickel, the oxide (JP,55-138,131,A.) containing at least one sort of elements chosen from Cu, Mo, and

W 58-220,362, 62-256,371, 62-90,863, 62-264,560, 63-114,065, 63-121,258, 63-211,565, 62-176,054, etc. are mentioned. Alkaline metals (element of the 1st (IA) fellows of the periodic table and the 2nd (IIA) fellows) other than lithium and/or aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be contained. 0-30-mol% of a mixed amount is desirable to a transition metal.

[0042]The still more desirable thing as lithium containing transition metal multiple oxide positive active material used by this invention, It is the material which has the Spinel structure expressed with the material or $LiyMn_2O_4$ (more than [y= 0.02 or less / 2]) containing Li_xMO_2 (at least one sort of atoms chosen from M=Co, nickel, Fe, and Mn, and 1.2 or less [x= 0.02 or more]). As for the former, Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, $Li_xCo_jnickel_{1-j}O_2$ (it is x= 0.02-1.2 and j= 0.1-0.9 here), etc. are specifically mentioned. Here, the above-mentioned x value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.

[0043]A conducting agent, binder, and filler other than an active material substance are added by the electrode compound of this invention. In the constituted cell, if a conducting agent is a electron conductive material which does not cause a chemical change, it is [anything] good. Usually, natural graphite (flaky graphite, scaly graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, Ketchen black, carbon fiber, and a metal powder (copper.) Conductive materials, such as a metal fiber or polyphenylene derivatives (JP,59-20,971,A), such as nickel, aluminum, and silver (JP,63-148,554,A), can be included as one sort or these mixtures. Especially concomitant use of black lead and acetylene black is preferred. As for the addition, 1 to 50 % of the weight is preferred, and its 2 to 30 % of the weight is especially preferred. In carbon or especially black lead, 2 to 15 % of the weight is preferred.

[0044]Although an aprotic organic solvent and lithium salt are used as a binder for holding an electrode compound in this invention, Fluorocarbon rubber, an ethylene-propylene-diene terpolymer (EPDM) with compatibility with an electrolysis solution, Polymer, such as a polyvinyl pyrrolidone, an ethylene-propylene-diene terpolymer (EPDM), styrene butadiene rubber, and polybutadiene, etc. can use as one sort or these mixtures. As for the addition of the binder, 1 to 30 % of the weight is preferred, and its 2 to 10 % of the weight is especially preferred.

[0045]In the constituted cell, a filler can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, are used. Although the addition in particular of a filler is not limited, 0 to 30 % of the weight is preferred.

[0046]The electronic conductor which does not cause a chemical change in the constituted cell as a charge collector of right and a negative electrode is used. As a charge collector of an anode, aluminum and an aluminum alloy have the desirable especially preferred thing which made the surface of aluminum or stainless steel else [, such as aluminum, stainless steel, nickel and titanium,] process carbon, nickel, titanium, or silver. As a charge collector of a negative electrode, copper or a copper alloy has desirable especially preferred copper, stainless steel, nickel, and titanium.

[0047]Although the thing of a film sheet shaped is usually used, what was netted and punched, the Russ object, a porous body, foam, the Plastic solid of a textiles group, etc. can be used for the shape of a charge collector. Although thickness in particular is not limited, it is 1-500 micrometers. As for a collector surface, it is also desirable to attach unevenness by a surface treatment.

[0048]As a coating method, the reverse roll method, the Dailekh trawl method, the braid method, the knife

method, the extrusion method, the curtain method, the photogravure method, the bar method, a dip method, and the squeeze method can be mentioned, for example. The braid method, the knife method, and the extrusion method are preferred also in it. As for spreading, it is preferred to carry out the speed for 0.1-100-m/. Under the present circumstances, according to the solution physical properties of a mixture, and drying property, the surface state of a good coating layer can be acquired by selecting the above-mentioned coating method. The time of one side [every] ** or double-sided coincidence may be sufficient as spreading.
[0049]Continuation, an intermission, or a stripe may be sufficient as spreading. Although the thickness, length, and width of the coating layer are decided with the shape and the size of a cell, the thickness of the coating layer of one side is in the compressed state after dry, and its 1-2000 micrometers are preferred.
[0050]the method which it was independent or was combined is used for desiccation of an electrode sheet coated article and a dehydration method for a hot wind, a vacuum, infrared rays, far-infrared rays, an electron beam, and a damp wind -- things can be carried out. The range of drying temperature of 80-350 ** is preferred, and its range which is 100-250 ** is especially preferred. 2000 ppm or less of water content are preferred by the whole cell, and it is preferred to use 500 ppm or less in positive electrode mixture, negative electrode mixture, or an electrolyte, respectively. Although the method generally adopted can be used for the method of pressing a sheet, it is preferred. [of especially the calendar pressing method] Although press pressure in particular is not limited, its 0.2 - 3 t/cm^2 is preferred. As for the pressing speed of the calendar pressing method, the amount of 0.1-50-m/is desirable, and room temperature -200 ** of press temperature is preferred. As for the ratio of negative electrode sheet width to a positive electrode sheet, 0.9-1.1 are preferred, and 0.95-especially 1.0 are preferred. The content ratio of positive active material and a negative pole material changes with a compound kind or mixture formulas.
[0051]The separator of this invention needs to have a function which blockades the above-mentioned crevice above 80 ** for safety reservation, raises resistance, and intercepts current, and it is preferred that blockade temperature is not less than 90 ** and 180 ** or less.
[0052]The shape of the hole of a separator is usually a round shape and an ellipse form, a size is 0.05 micrometer to 30 micrometers, and its 0.1 to 20 micrometers are preferred. It may be a hole of rod form or an infinite form like [at the time of furthermore making by the extending method and a phase separation method]. It is 20% to 90%, the ratio, i.e., the porosity, which these crevices occupy, and it is desirable. [35 to 80% of] These separators may be single materials, such as polyethylene and polypropylene, or may be two or more sort composite-ized material. Especially the thing that laminated two or more sorts of microporous film into which an aperture, porosity, the blockade temperature of the hole, etc. were changed especially is preferred.
[0053]The steel board with which the battery can and battery lid which can be used by this invention performed the nickel plate as construction material, a stainless steel plate (SUS304, SUS304L, and SUS304N.) It is SUS316, SUS316L, SUS430, SUS444 grade, the stainless steel plate (same as the above) that performed the nickel plate, aluminum or its alloy, nickel, titanium, and copper, and is round shape tubed, ellipse form tubed one, square tubed, and rectangle tubed as shape. Especially when an armor can serves as a negative pole terminal, a stainless steel plate and the steel board which performed the nickel plate are preferred, and when an armor can serves as a positive pole terminal, a stainless steel plate, aluminum, or its alloy is preferred. Any, such as a button, coin, a sheet, a cylinder, and an angle, may be sufficient as the shape of a battery can.

[0054]In order to prevent the internal pressure rise and run away reaction by an anomalous reaction within a cell, it is preferred to incorporate a valve element and a current cutoff element. It is more desirable when it includes in an obturation part combining the current cutoff switch which operates corresponding to displacement of the valve element which a valve is destroyed by the obturation part by an internal pressure rise, and opens internal pressure especially, and a valve element. These pressure induction valve elements and current cutoff switches can use what is indicated to a JP,2-112151,A publication before examination, a 2-288063 publication before examination, a 6-215760 publication before examination, a 9-92334 publication before examination, etc. In addition, it may be equipped with various safety elements (for example, a fuse, bimetal, a PTC element, etc.) known from the former.

[0055]Metal (for example, iron, nickel, titanium, chromium, molybdenum, copper, aluminum, etc.) with electrical conductivity and those alloys can be used for the lead board used by this invention. A publicly known method (electric welding of an example, a direct current, or exchange, laser welding, ultrasonic welding) can be used for the welding process of a battery lid, a battery can, an electrode sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0056]Metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metal or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used.

[0057]As construction material, they are olefin system polymer, fluorine system polymer, cellulose type polymer, polyimide, and polyamide, from organic solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has preferred olefin system polymer, and especially its polymer of a propylene subject is preferred. It is preferred that it is block copolymerization polymer of propylene and ethylene.

[0058]Although the use in particular of the nonaqueous secondary battery of this invention is not limited, when it carries in electronic equipment, for example, A notebook computer, a pen input personal computer, a mobile personal computer, an Electronic Book player, A cellular phone, a cordless phone cordless handset, a pager, a handy terminal, Portable fax, a portable copy, a portable printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, a mini disc, an electric shaver, a transceiver, an electronic notebook, a calculator, memory card, a portable tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, as a noncommercial use, a motor, a light, a toy, a game machine machine, a load conditioner, a clock, a stroboscope, a camera, medical equipment (a pacemaker, hearing aid, and a shoulder are also ****s etc.), etc. are mentioned. A solar cell and combination are also made.

[0059]

[Example]Although an example is raised to below and this invention is explained in more detail, unless the main point of an invention is exceeded, this invention is not limited to an example.

[0060][Example of Li foil pasting multilayer negative electrode sheet creation-1] natural graphite (C-1) -- as 190 g and a conducting agent, 9 g was kneaded for polyvinylidene fluoride as the artificial graphite 30g and a binder, 500 ml of N-methyl pyrrolidone was kneaded as a medium, and the negative electrode mixture slurry was obtained. Next, it mixed at a rate of alpha-alumina 45 weight section, graphite 7 weight section, polyvinylidene fluoride 3 weight section, and N-methyl-pyrrolidone 100 weight section, and the auxiliary layer

slurry was obtained. The negative electrode mixture slurry was used as the lower layer, it painted on both sides of 18-micrometer-thick copper foil using the braid coating machine by having made the auxiliary layer slurry into the upper layer, compression molding was carried out with the roller press machine after 150 ** desiccation, and the negative electrode sheet precursor with a 136 micrometer[in thickness] x width of 55 mm was created. After cutting this in length of 540 mm, after welding the lead board made from nickel to an end, heat treatment was performed for 1 hour using the far infrared heater at 230 ** in dry air not more than dew point-40 **. Five stripe shape lithium foil (99.8% of purity) with a thickness of 35 micrometers respectively judged in 4 mm[in width] x length of 52 mm to both sides of the negative electrode sheet precursor after heat treatment was stuck on the length and the right angle of a negative electrode sheet precursor at intervals of 90 mm, and was used as them, and negative electrode sheet ANL-1 shown in Table 1 was created.

[0061][Example of Li foil pasting multilayer negative electrode sheet creation-2] Change to natural graphite (C-1), and A material given in JP,5-182,664,A (C-2), The microfilament material which calcinated the MEZOFESU pitch of the statement to JP,7-85,862,A (C-3), Using vapor-phase-epitaxy carbon (C-4) given in JP,63-58,763,A, like example of Li foil pasting multilayer negative electrode sheet creation-1, create a negative electrode sheet precursor and the lead board made from nickel to an end in a similar manner Welding, Lithium foil (99.8% of purity) was carried out to the length and the right angle of the negative electrode sheet precursor, it stuck on stripe shape, and negative electrode sheet ANL-2 shown in Table 1, and 3 and 4 were created.

[0062][The example of multilayer negative electrode sheet creation which does not stick Li foil] Negative electrode sheet AN-1 for cells of the comparative example mentioned later, and 2, 3 and 4 were created. Namely, after cutting a negative electrode sheet precursor with an example of Li foil pasting multilayer negative electrode sheet creation-136-micrometerx width of 55 mm in length of 540 mm, [which carried out compression molding by 1 and 2] [in thickness] Negative electrode sheet AN-1 shown in Table 1, and 2, 3 and 4 were used without having heat-treated for 1 hour using the far infrared heater at 230 ** in dry air not more than dew point-40 **, and sticking lithium foil, after welding the lead board made from nickel to an end.

[0063]

[Table 1]

表1

負極シート	材料番号	負極材料	Li箔貼付重量mg：負極シート両面
ANL-1	C-1	天然黒鉛	37
2	2	難黒鉛化性炭素材料	37
3	3	メゾフェースピッチ系炭素材料	37
4	4	気相成長炭素	37
AN-1	C-1	天然黒鉛	0
2	2	難黒鉛化性炭素材料	0
3	3	メゾフェースピッチ系炭素材料	0
4	4	気相成長炭素	0

[0064][Example of positive electrode sheet creation-1] Positive-active-material $LiCoO_2$ 200g and 10 g of

acetylene black were mixed with the homogenizer, 5 g of poly **-ized vinylidene was continuously mixed as a binder, 500 ml of N-methyl-2-pyrrolidone was added, kneading mixing was carried out, and the positive electrode mixture paste was created. Compression molding of the positive electrode mixture paste was carried out to both sides of the 30-micrometer-thick aluminium foil charge collector with the roller press machine after spreading and 150 ** desiccation by the braid coating machine, it judged in the predetermined size, and the band-like positive electrode sheet was created. Furthermore, drying desiccation was enough carried out with the far infrared heater all over the dry box (dew point; dry air not more than -50 **), after cutting this in length of 495 mm, the lead board made from aluminum was welded to the end, and a positive electrode sheet 165 micrometers in thickness, and [53.5 mm/ in width / x/ 495 mm] in length was produced (CA-1).

[0065][Example of electrolysis solution creation-1] Next, 65.3 g of diethyl carbonate was put into the polypropylene container of a 200-cc thin mouth by argon atmosphere, and 22.2 g of ethylene carbonate [a small amount of] was dissolved every, taking care that solution temperature does not exceed 30 ** to this. Next, dissolving 0.8 g of 1,2-bis(ethoxycarbonyl)-1,2-dimethylhydrazine, and being careful of 0.4 g $LiBF_4$ and 12.1-g $LiPF_6$ for solution temperature not to exceed 30 ** subsequently. It dissolved in the above-mentioned polypropylene container every in small quantities in order, respectively. The obtained electrolysis solution was a water-white fluid by specific gravity 1.135 (table 2:S11). The amount of [18 ppm (it measures with a product made from Kyoto electron trade name MKC-210 type Carl Phi Shah water measurement device) and] free acid of moisture was 24 ppm (the bromthymol blue is used as an indicator, and using a decinormal NaOH aqueous solution, a neutralization titration is carried out and it measures).

[0066][Example of electrolysis solution creation-2] Seven sorts of electrolysis solutions S12 as follows shown in Table 2 in the same procedure as example of electrolysis solution creation-1, and 13, 14, 15, 16, 17 and 18 were produced.

[0067][The example for comparative examples of electrolysis solution creation] Three sorts of electrolysis solutions S21 which do not contain the additive agent of this invention, and 25 and 28 (Table 2) were produced as an electrolysis solution for the below-mentioned comparative examples.

[0068]

[Table 2]

表2

電解液No.	溶媒			添加剤		リチウム塩	
	DEC (g)	EC (g)	PC (g)	材料	(g)	$LiBF_4$ (g)	$LiPF_6$ (g)
S11	63.5	22.2	—	1,2-ビス(エトキシカルボニル)-1,2-ジメチルヒドラジン	0.8	0.4	12.1
12	〃	〃	—	1,2-ビス(エトキシカルボニル)-1,2-ジメチルヒドラジン／ベンゾフラン	0.4/0.4	0.4	12.1
13	〃	〃	—	ベンゾフラン	1.6	—	12.5
14	〃	〃	—	ベンゾチオフェン	0.8	0.4	12.1
15	〃	11.1	11.1	アクリジン	〃	〃	〃
16	〃	〃	〃	ｶﾃｺｰﾙｶｰﾎﾞﾈｰﾄ	〃	〃	〃
17	〃	〃	〃	〃	1.6	〃	〃
18	〃	—	22.2	〃	〃	〃	〃
S21	63.5	22.2	—	—	—	0.4	12.1
25	〃	11.1	11.1	—	—	〃	〃
28	〃	—	22.2	—	—	〃	〃

表中の略称 DEC：ジエチルカーボネート
EC：エチレンカーボネート
PC：プロピレンカーボネート

[0069][Example-1] How to make a cylindrical cell is explained according to drawing 1 which is the key map. Li foil pasting multilayer negative electrode sheet and the positive electrode sheet carried out drying desiccation at 230 ** in dry air not more than dew point-40 ** for 30 minutes, respectively. In dry atmosphere, it laminated in the separator made from a positive electrode sheet (CA-1) drying dried (1) microporous polyethylene film (3), Li foil pasting multilayer negative electrode sheet (ANL-1) (2) of ending with drying dry, and order that is a separator (3) further, and this was wound spirally. It stored to the iron closed-end cylindrical battery can (4) which performed the nickel plate which serves this wound electrode group as a negative pole terminal. The electrolysis solution (S11) created in the example of electrolysis solution creation was poured into the battery can. the battery lid which has a positive pole terminal -- a gasket (6) -- passing -- the cylindrical cell (B-1) was created in total. The battery lid (5) used as a positive pole terminal connected beforehand the positive electrode sheet (1) and the battery can (4) with the negative electrode sheet (2) with the lead terminal. (7) is a safety valve. After neglecting it for seven days at 40 ** after this, the following quality assessment was performed.

[0070]The produced cylindrical shape cell (B-1) is charged by 1.2A at ordinary temperature. In this case, it charges by constant current to 4.2V, and charge controls charging current to keep it constant by 4.2V until 2.5 hours pass since charge starting. Discharge was carried out according to constant current to 2.8V by 1.2A. The ratio of charging capacity to the service capacity in this case is made into coulomb efficiency. Then, on the same charge-and-discharge conditions, carry out charge and discharge with the charge final voltage 4.2V and the discharge final voltage 2.8V and 1.2A, and let the value of the 5th cycle at that time be service capacity. It is considered as the capacity maintenance rate of the 200 cycle eye which repeated charge and

discharge. The result of the capacity maintenance rate of coulomb efficiency, service capacity, and a 200 cycle eye is shown in Table 3.

[0071][Example-2] The cylindrical cell B-2-12 which combined Li foil pasting multilayer negative electrode sheet, the positive electrode sheet, and the electrolysis solution as shown in Table 3 is created like example-1, and the result of the capacity maintenance rate of coulomb efficiency, service capacity, and a 200 cycle eye is shown in Table 3.

[0072]

[Table 3]

表3

電池番号	負極シート	正極シート	電解液	クーロン効率	放電容量(mAh)	200 ｻｲｸﾙ容量維持率(%)
B-1	ANL-1	CA-1	S11	0.98	1700	87
2	2	〃	〃	0.94	1570	80
3	3	〃	〃	0.96	1670	88
4	4	〃	〃	0.97	1650	85
5	ANL-1	〃	S12	0.99	1720	84
6	2	〃	13	0.97	1520	86
7	3	〃	12	0.98	1680	82
8	4	〃	14	0.94	1640	78
9	ANL-1	〃	15	0.96	1650	85
10	〃	〃	16	0.95	1690	83
11	〃	〃	17	0.93	1670	86
12	〃	〃	18	0.92	1660	88

[0073][Comparative example-1] Using a negative electrode sheet (AN-1), like example-1 A microporous polyethylene film separator, After creating cylindrical cell BR-1 which combined the positive electrode sheet with a 53.5 mm[in width] x length of 495 mm, and the electrolysis solution (S21) in dry atmosphere, the result of having evaluated the capacity maintenance rate of coulomb efficiency, service capacity, and a 200 cycle eye by example-1 and the conditions is shown in Table 4.

[0074][Comparative example-2] Using negative electrode sheet AN-1, like example-1 A microporous polyethylene film separator, Cylindrical cell BR-2 which combined the positive electrode sheet with a 53.5 mm [in width] x length of 495 mm and the electrolysis solution in dry atmosphere as shown in Table 4 - 7 are created, and the result of having evaluated the capacity maintenance rate of coulomb efficiency, service capacity, and a 200 cycle eye is shown in Table 4.

[0075]

[Table 4]

表4

電池番号	負極シート	正極シート	電解液	クーロン効率	放電容量(mAh)	200 サイクル容量維持率(%)
BR-1	AN-1	CA-1	S11	0.84	1530	83
2	〃	〃	15	0.80	1485	83
3	〃	〃	18	0.78	1500	86
4	AN-1	CA-1	25	0.41	660	—
5	〃	〃	28	0.38	580	—
BR-6	ANL-1	CA-1	S21	0.94	1620	82
7	〃	〃	25	0.48	820	—

[0076]The cell (B-1) of Example 1 of the electrolysis solution use which contains at least one sort of hydrazine derivatives, and/or aromatic compounds as Li foil pasting multilayer negative electrode sheet and the additive agent of this invention, If the performance of the cell (BR-1) of comparative example-1 is compared, coulomb efficiency will improve and service capacity will improve about 10%. Comparison of the performance of the cell (BR-2, 3) of the comparative example 2 of the cell (B-2 to B-12) of Example 2 will accept improvement in coulomb efficiency and service capacity similarly.

[0077]Although coulomb efficiency and service capacity improve from BR-1 of the comparative example 2, and 2 and 3, cell BR-6 as example-1 of this invention with same outside of using S21 in which the electrolysis solution does not contain a hydrazine derivative and/or aromatic compounds of comparative example-2 which is composition, The cell (B-1) of Example 1 is not attained to, but it is shown that it is required for improvement in service capacity to use together Li foil pasting multilayer negative electrode sheet and the electrolysis solution which contains at least one sort of hydrazine derivatives and/or aromatic compounds as an additive agent.

[0078]In order to improve the low-temperature characteristic of a cell, when electrolysis solution S15-18 which transposed a part of ethylene carbonate currently used as an electrolysis solution solvent to propylene carbonate, S25, and 28 are used, As opposed to not being remarkable by the cell (B-9-12) of example of experiment-2 as for the fall of coulomb efficiency and service capacity, By the cell (BR-4, 5, 7) of comparative example-2, coulomb efficiency and service capacity are falling remarkably (it became impossible [charge and discharge] by a 200 cycle eye), and contain propylene carbonate in an electrolysis solution, and the effect of the electrolysis solution additive agent of a nonaqueous secondary battery that a negative pole material is natural graphite is shown.

[0079]The same effect was acquired even if it changed positive-active-material $LiCoO_2$ into $LiNiO_2$ or $LiMn_2O_4$.

[0080]

[Effect of the Invention]By this invention, the nonaqueous secondary battery of the high capacity which supported lithium beforehand into carbon negative electrode material can be provided.

[Translation done.]